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DEXTRAN

Dextrans are a class of polysaccharides (qv) synthesized from sucrose by bacterial enzymes (dextransucrases, glucansucrases, or glucosyltransferases) to give D-glucans with contiguous α-1→6 glucosidic linkages in the main chains and a variable amount of α-1→2, α-1→3, or α-1→4 branch linkages. Pasteur is reported to have investigated dextran in 1861 (1), and Scheubler determined its empirical formula and named it dextran in 1874 (2). The formation of dextran was recognized as the result of the transformation of sucrose solutions into viscous solutions, gels, and precipitated flocculent material (3). Dextran has plagued humans as a contaminant in food preparations containing sucrose. For example, it can be produced by contaminating bacteria in wine, root beer, canned fruit, fruit juice, and sugar-cured hams, (4,5). Dextran presents a problem in the sugar-refining industry where it plugs process pipes and filters, inhibits crystallization, reduces the yield, and distorts optical rotation measurements used in the standardization and determination of sucrose purity. About 1970, dextran was also recognized to be the principal component of dental plaque and to be involved in the development of dental caries (6,7). Dextrans and dextran derivatives, however, have found valuable uses as blood plasma substitutes, molecular sieves, anticoagulants, food additives, explosives, high viscosity gums, and several other applications.

The synthesis of dextran from sucrose by a cell-free bacterial culture was first demonstrated in 1940 (8). The two principal genera of bacteria that produce the enzymes that synthesize dextrans are *Leuconostoc* and *Streptococcus*. These genera are gram-positive, facultatively anaerobic cocci closely related to each other. However, the *Leuconostoc* species require sucrose in the culture medium as an inducing agent for the elaboration of glucansucrase, whereas the *Streptococcus* species do not require sucrose to elaborate glucansucrase. The glucansucrases of the *Leuconostocs* are inducible and the glucansucrases of the *Streptococci* are constitutive.

A study of the dextrans produced by 96 *Leuconostocs* and *Streptococci* has been made (9). The polysaccharides were characterized by periodate oxidation and their physical properties. It was found that the polysaccharides had a relatively high amount of α-1→6 linkages with varying amounts of α-1→2, α-1→3, and α-1→4 linkages, depending on the strain of organism. A drawback of the periodate method was that the α-1→3 and α-1→4 linkages could not be distinguished. The definitive nature of the branch linkages in many of these dextrans was later determined by methylation analyses (see Table 1). The alcohol precipitates were described in various qualitative terms such as pasty, fluid, stringy, tough, long, short, flocculent, etc, which suggested differences in structure. Some strains produced water-insoluble polysaccharides and some formed more than one kind of polysaccharide.

Differential alcohol fractionation clearly separated two different polysaccharides produced by certain strains (10). In many cases, the first polysaccharide was precipitated by 36–37% alcohol and was designated as the L fraction for less soluble, ie, precipitated at a lower alcohol concentration than the second fraction. The second polysaccharide precipitated by 40–44% alcohol was designated the S fraction for more soluble. The differential alcohol-precipitation curves for four different *Leuconostoc mesenteroides* strains are shown in Figure 1. The B-512F

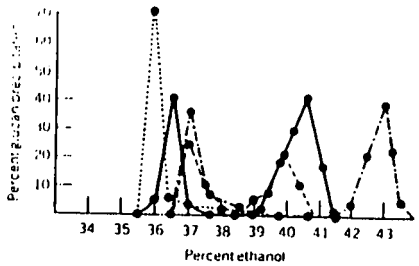

Fig. 1. Differential alcohol precipitation of glucans from four strains of *Leuconostoc mesenteroides*: ····, B-512F; ——, B-1355, – – –, B-1299; and –·–·–, B-742.

strain gave a single polysaccharide, whereas strains B-1355, B-742, and B-1299 each gave two polysaccharides. The two alcohol-precipitated polysaccharides of these three strains had characteristically different appearances. This was most pronounced for the two B-1355 polysaccharides in which the L fraction was a translucent gel and the S fraction a heavy, opaque, white precipitate (11) (see Fig. 2). The differences in the alcohol concentration needed to precipitate the two glucans and the striking differences in the appearance of the precipitates is indicative of differences in their structures.

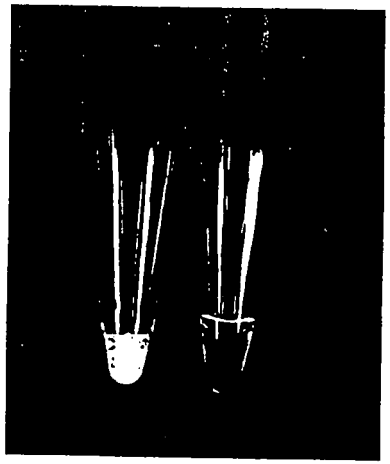

Fig. 2. Ethanol precipitates from *Leuconostoc mesenteroides* B-1355 glucansucrase reaction digests. S = alternan and L = dextran.

The organism (*L. mesenteroides* B-512F) is mass cultured as for ordinary dextran production (62). The cells are removed and the dextran is precipitated with organic solvents. The precipitated dextran is redissolved and hydrolyzed with hydrochloric acid at 100–105°C. The course of the hydrolysis is followed by viscosity measurements from which an optimum end point is obtained. The hydrolysis is stopped by cooling and neutralization of the acid. The solution after hydrolysis contains dextran with molecular weights ranging from a few hundred to one million. The mixture is fractionally precipitated with organic solvents to give a clinical dextran with a molecular weight of 25,000–200,000. Fractionation procedures are repeated to give material with a narrow molecular weight as required (see also FRACTIONATION). The final solution is deionized in a mixed-bed deionizing column and the volume is reduced by evaporation; spray-drying gives a free-flowing, white powder with an average particle size of 40 μm and an average molecular weight of 75,000 daltons (62).

Dextran produced by *L. mesenteroides* B-512F is the material of choice for clinical dextran because it has a low degree of antigenicity and a high percentage (95%) of α-1→6 glycosidic linkages. The latter is important as the enzymes in the human body can only slowly hydrolyze the α-1→6 linkages in contrast with α-1→4 linkages of starch and glycogen, which are rapidly hydrolyzed by human α-amylases. Furthermore, the α-1→6 linkage imparts high water solubility to the molecule in contrast with material having α-1→3 linkages or β-linkages. Thus, B-512F dextran has the low antigenicity, high water solubility, and high biological stability in the human blood stream required for a suitable blood-plasma substitute. Clinical dextran is not, however, routinely used today as a blood-plasma substitute because approximately 20% of the population would have an anaphylatic response. Nevertheless, during a disaster, when blood plasma is scarce, clinical dextran as a blood-plasma substitute might save lives.

Derivatives and Uses

Many different types of esters and ethers of dextran provide macromolecules with diverse properties and negative, positive, or neutral charges. Properties depend upon the type of substituent, the degree of substitution, and the molecular weight of the dextran.

Cross-linked Dextran. The most widely used dextran derivative is obtained by the reaction of an alkaline solution of dextran with epichlorohydrin to give cross-linked chains. The product is a gel that is used as a molecular sieve. With its commercial introduction in 1959 by Pharmacia Fine Chemicals, Ltd., Uppsala, Sweden, cross-linked dextran revolutionized the purification and separation of biochemically important macromolecules such as proteins, nucleic acids, and polysaccharides.

Commercial cross-linked dextran is known as Sephadex. It is produced in bead form by dissolving the dextran in sodium hydroxide solution, dispersing it in an immiscible organic solvent such as poly(vinyl acetate) in toluene, and adding epichlorohydrin. The reaction mixture is kept at 50°C until the beads gel (67,68). Several types of Sephadex have been developed, eg, the G-series (G-10 to G-200), with different degrees of cross-linking, giving different molecular exclusion limits. The G-numbers actually refer to the amount of water absorbed by the dry beads. Sephadex G-10, the highest cross-linked material, regains about 1 mL water/g of dry gel, and Sephadex G-200, the lowest cross-linked material, has a water regain of about 20 mL/g of dry gel. The gels are available in particle sizes from ca 37–300 μm (50 to <400 mesh). Each Sephadex type achieves separation within a particular molecular weight range, which depends upon the average pore size of the gel. Molecules of a molecular weight above the upper limit of the range, the exclusion limit, are excluded from the gel and emerge from the gel column in the void volume. Molecules with molecular weights below the exclusion limit are fractionated according to size with the larger molecules emerging first (see Table 3). Cross-linked dextran matrix has also been used as a solid support for affinity chromatography in which the desired-affinity ligand is covalently coupled to the dextran by adding alkaline cyanogen bromide to the cross-linked dextran followed by the ligand (69,70) (see CHROMATOGRAPHY, AFFINITY).

Table 3. Properties of Sephadex*

Sephadex type	Dry particle diameter, μm	Fractionation range, mol wt: Peptides and globular proteins	Fractionation range, mol wt: Dextrans	Bed volume mL/g dry Sephadex	Protein exclusion limit, mol wt
G-10	40–120	up to 700	up to 700	2–3	700
G-15	40–120	up to 1,500	up to 1,500	2.5–3.5	1,500
G-25		1,000–5,000	100–5,000	4–6	5,000
coarse	100–300				
medium	50–150				
fine	20–80				
superfine	10–40				
G-50		1,500–30,000	500–10,000	9–11	30,000
coarse	100–300				
medium	50–150				
fine	20–80				
superfine	10–40				
G-75	40–120	3,000–70,000	1,000–50,000	12–15	70,000
superfine	10–40				
G-100	40–120	4,000–150,000	1,000–100,000	15–20	150,000
superfine	10–40				
G-150	40–120	5,000–400,000	1,000–150,000	20–30	300,000
superfine	10–40			18–22	
G-200	40–120	5,000–800,000	1,000–200,000	30–40	600,000
superfine	10–40			20–25	

* From manufacturers' technical information.

Ionic groups, such as diethylaminoethyl (DEAE) and carboxymethyl (CM), attached to dextran and cross-linked dextran give anionic and cationic dextrans and ion-exchange molecular sieves. The addition of DEAE-dextran to agar overlays greatly enhances plaque formation by virus (71) and is related to the presence of sulfated polysaccharides in agar, which inhibits plaque formation by some viruses (72); the DEAE-dextran interacts with these sulfated polysaccharides.

Dextran Sulfate. The sulfate ester of dextran may be prepared by mixing chlorosulfonic acid in pyridine at −10°C, raising the temperature to 60°C, and adding dry, finely powdered dextran. The product has 1 to 2 sulfate groups per

glucose residue. Dextran sulfate has anticoagulant properties similar to, although less effective than that of heparin, a naturally occurring polysaccharide containing carbohydrate sulfate esters. A certain minimum number of sulfate groups per glucose residue of dextran is required for anticoagulant activity. The activity increases sharply between 1.0 and 1.3 sulfate groups per glucose residue. The sulfate content of heparin is 1.5 sulfate groups per monomer unit (73).

High molecular weight dextran sulfate is toxic because it precipitates fibrinogen resulting in embolism of the blood vessels. The toxicity is greatly reduced, however, by a drastic reduction in the molecular weight to 20,000 daltons, which approximates the molecular weight of heparin (17,000 daltons). Good anticoagulant activity with low toxicity has been obtained with a dextran sulfate of 7,300 mol wt and 1.9 sulfate groups per glucose residue (73).

Dextran sulfate differs greatly from dextran by being a polyanion surrounded by a cloud of cations, eg, Na^+, which may be exchanged for other counter cations with a greater affinity for sulfate. The addition of Ca^{2+}, Ba^{2+}, or Sr^{2+} to a solution of sodium dextran sulfate results in the formation of insoluble calcium, barium, or strontium polysalts. The interaction of dextran sulfate with cationic detergents, eg, cetylpyridinium chloride, varies with the number of sulfate groups and has been used to fractionate dextran sulfates according to their sulfate content (74).

Dextran sulfate interacts with β-lipoproteins and as such has found applications in analytical and preparative procedures. A micromethod for the determination of serum cholesterol (75) and turbidometric methods for β-lipoproteins (76,77) have been developed. Precipitation of β-lipoproteins by dextran sulfate from IgM antibody preparations improved the purification procedure for IgM (78).

Dextran sulfate has an affinity for sites that bind nucleic acids and is a potent inhibitor for ribonuclease (79). It has been used in the preparation and purification of polyribosomes (80), the release 45S RNA from cell nuclei lysates (81), the release of DNA from DNA-histone complexes (82), and the inhibition of t-RNA binding to ribosomes (83).

In contrast with DEAE-dextran, which enhances virus infections on agar plates (70), dextran sulfate inhibits virus infections. Dextran sulfate binds attenuated polio virus and interferes with its initial adsorption to susceptible cells (84). Strain differences of virus inhibition by dextran sulfate have been used to study differences in viruses (85,86) and to make correlations with their virulence (87).

Mercaptodextran. Mercaptodextran may be synthesized by thiolating dextran with *N*-acetyl homocysteine thiolactone. The thiol groups are unusually stable toward autooxidation but are highly reactive and readily reduce disulfide bonds. Mercaptodextran has a higher affinity for heavy metal ions, such as silver, mercuric, cupric and auric ions, than most other thiols and chelating agents, eg, glutathione, cystamine, diethyldithiocarbamate, and ethylenediaminetetraacetic acid. The Hg-mercaptodextran stability constant is about 10^{20}. High affinity for heavy-metal ions, combined with low toxicity, suggests possible uses in acute, heavy-metal poisoning and in environmental cleanup of heavy-metal contamination (88).

Many other derivatives such as carbonates, triacetates, palmitates, phosphates, nitrates, and benzyl and hydroxyalkyl ethers have been reported with a wide range of uses as tableting and encapsulating agents, emulsifying and thickening agents, high viscosity gums, explosives, soil conditioners, well drilling, etc (89).

Dental Plaque and Tooth Decay

The principal sugar-producing tooth decay is sucrose (90), and the principal organism found in dental caries is *Streptococcus mutans* (91). The *S. mutans* produces two glucansucrases (glucosyltransferases), which react with sucrose to form two types of glucans, a water-insoluble glucan (mutan) and a water-soluble glucan (dextran). Together these two polysaccharides make up dental plaque that adheres to the enamel of the teeth, holding myriads of *S. mutans* cells in close proximity to the enamel; the polysaccharides also provide an anaerobic environment for the bacteria. The two glucansucrases polymerize the glucose moiety of sucrose into dental plaque and simultaneously release an equivalent amount of D-fructose. The fructose is metabolized further by the bacteria through anaerobic glycolysis to D-lactic acid, which, because of the plaque, is held in close contact with the enamel of the teeth. The acid concentration builds up around the teeth and attacks the enamel resulting in dental lesions (92).

BIBLIOGRAPHY

"Dextran" in *EPST* 1st ed., Vol. 4, pp. 805–824, by Allene Jeanes, Northern Regional Research Laboratory, U.S. Department of Agriculture.

1. L. Pasteur, *Bull. Soc. Chim. Paris*, 30 (1861).
2. C. Scheubler, *Z. Ver. Dtsch. Zucker-Ind.* 24, 309 (1874).
3. M. E. Durin, *Compt. Rend.* 83, 128 (1876).
4. F. W. Fabian and R. H. Henderson, *Food Res.* 15, 415 (1950).
5. R. H. Deibel and C. F. Niven, *Appl. Microbiol.* 7, 138 (1959).
6. B. Krasse, *Arch. Oral Biol.* 10, 223 (1965).
7. S. B. Banghart, *Arch. Oral Biol.* 12, 11 (1967).
8. E. J. Hehre, *Science* 93, 237 (1941).
9. A. Jeanes, W. C. Haynes, C. A. Wilham, J. C. Rankin, E. H. Melvin, M. J. Austin, J. E. Cluskey, B. E. Fisher, H. M. Tsuchiya, and C. E. Rist, *J. Am. Chem. Soc.* 76, 5041 (1954).
10. C. A. Wilham, B. H. Alexander, and A. Jeanes, *Arch. Biochem. Biophys.* 59, 61 (1955).
11. G. L. Côté and J. F. Robyt, *Carbohydr. Res.* 101, 57 (1982).
12. M. A. McCalip and H. H. Hall, *International Association of Sugar Cane Technology Proceedings of the 6th Congress 1938*, 1939, pp. 986–1004.
13. R. Moroz in P. Honig, ed., *Principles of Sugar Technology*, Vol. 3, Elsevier Publishing Co., Amsterdam, 1963, p. 373.
14. J. Carlsson, G. Soderholm, and I. Almfeldt, *Arch. Oral Biol.* 14, 243 (1969).
15. J. D. de Stoppelar, J. Van Houte, and O. Backer-Dirks, *Caries Res.* 4, 114 (1970).
16. J. W. Van Cleve, W. C. Schaefer, and C. E. Rist, *J. Am. Chem. Soc.* 78, 4435 (1956).
17. F. R. Seymour, R. D. Knapp, and S. H. Bishop, *Carbohydr. Res.* 51, 179 (1976).
18. F. R. Seymour, M. E. Slodki, R. D. Plattner, and A. Jeanes, *Carbohydr. Res.* 53, 153 (1977).
19. F. R. Seymour, E. C. M. Chen, and S. H. Bishop, *Carbohydr. Res.* 68, 113 (1979).
20. F. R. Seymour, R. D. Knapp, S. H. Bishop, and A. Jeanes, *Carbohydr. Res.* 68, 123 (1979).